

THE ANALYST.

JUNE, 1894.

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS.

The usual Monthly Meeting of this Society was held on May 2nd at the rooms of the Chemical Society, Burlington House. In the absence of the President, Mr. Alfred H. Allen took the chair.

The minutes of the last meeting were read and confirmed.

The following gentlemen were duly elected: As Members, Edward M. Chaplin, Thompson's Yard, Westgate, Wakefield; B. Henry Gerrans, 47, Aubert Park, High-bury, N.; William Marshall, 15, West Street, Rochdale; and B. H. Mumby, M.D., Portsmouth.

Mr. Harvey then read the following paper:

A SIMPLE APPARATUS FOR THE EXTRACTION FOR ANALYSIS OF GASES DISSOLVED IN WATER.

By SIDNEY HARVEY.

Having been engaged for several months past in an investigation in which the daily estimation of the gases dissolved in water was called for, specially as regards the amount of free CO_2 present, I deemed it desirable to confirm the results, obtained by the ordinary gravimetric and titration method, by the actual measurement of the gases themselves.

In doing this I was perplexed by the complicated character and unsatisfactory performance of various forms of apparatus proposed for the purpose.

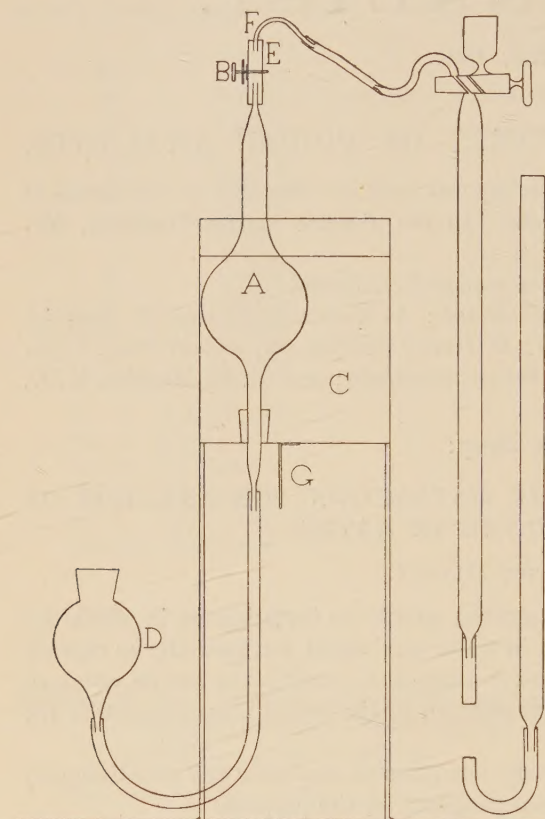
Among the drawbacks attending the use of these may be mentioned, the uncertainty as to the exact amount of water operated upon; the unavoidable escape of some of the water (when expanded) into some part of the apparatus where it fails to undergo efficient treatment; the use of steam to expel air from the apparatus at the outset, and the consequent inconvenience due to the presence of the condensed water therefrom, either into the gas receiver or elsewhere, favouring re-absorption and consequently low results; the number of junctions requiring careful securing against leakage.

After trying several forms of apparatus, I found one suggested by Thresh (*Journal Chemical Society*, Transactions, vol. xxxix., p. 399) to be the best for my purpose, but even in this ingenious arrangement I found it difficult to keep the perforated rubber stoppers secure throughout the operation. Profiting, however, by Dr. Thresh's suggestion, I ultimately constructed the present apparatus, which, while, no doubt, subject to criticism, has at least the merit of simplicity, and has proved very serviceable and manageable in my hands.

It consists of a globular, spindle-shaped glass vessel (A), having two opposite tapering necks, 13 to 14 inches long between extremities, the globular part $3\frac{1}{4}$ or $3\frac{1}{2}$ inches in diameter. The upper neck is somewhat enlarged, tapering gradually, the

lower is narrow and cylindrical; both end in a capillary bore with a swollen tip, in order that the rubber tubing may be securely affixed. The upper one has a short length of small-bore pressure tubing, securely tied and furnished with a screw clamp (B).

The apparatus is used as follows: In the first place the exact capacity of the vessel from end to end is ascertained once for all. It is then filled with the sample to be analyzed, the screw clamp (B) is closed, and the vessel carefully fixed upright in a tin water-bath (C) 6 inches diameter, 7 inches high, standing on legs 12 inches high, having an opening in the bottom closed by a perforated cork, and so arranged that while the lower stem of the spindle projects 2 inches below the bottom, the globular part is immersed in the bath itself.



The clamp is now opened, and about one-third of the water allowed to run out into a measured vessel. Of course, the amount deducted from the capacity of the globe when full gives the amount experimented upon. The lower end of the spindle has now two feet of small-bore pressure tubing slipped over it and secured. This tubing has a mercury reservoir (D) at the other end, and the latter suitably supported.

Clean pure mercury is now poured into the reservoir, the clamp (B) again opened, and the air, together with any bubbles, driven out, the water being allowed to follow to the upper end of the rubber tube (E). The clamp is now closed again. An ordinary nitrometer, having a bent capillary glass tube (F) affixed to the beak, is now filled with mercury, and the mercury forced to the end of the capillary tube, which is now thrust into the top of the rubber tubing and secured. The reservoir is now lowered, and the clamp cautiously opened in order to draw a little mercury sufficiently far to reach the lower end of the capillary tube. The clamp is now closed, the water-bath filled with cold water, and heat applied. To prevent the latter injuring the lower end of

the spindle, a metal curtain (g) is riveted on to the bottom of the bath so as to screen the glass from the flame, and for the same reason the hole in the bath is excentric to allow sufficient space for heating.

Under the diminished pressure caused by lowering the cistern, the water in the spindle soon boils vigorously, and, so far as my experience goes, without "bumping," and the expelled gases soon collect in the upper stem. After two hours' boiling, during which the process requires but little attention, the reservoir may be raised, the clamp (B) opened, the gases passed into the nitrometer, taking care not to let the "following water" rise as far as the capillary part of the spindle. The clamp is again closed, and the reservoir lowered, and the operation continued in order to see if any more gas appears. Finally the reservoir is raised, and the residual gas driven completely into the nitrometer, the "following water" being allowed this time to go as far as the nitrometer tap.

The apparatus is now disconnected from the nitrometer, the contents of which latter, after due interval, are subjected to measurement and absorption as usual.

The advantages claimed for the above apparatus are as follows: The water treated, together with the evolved gases, do not quit the vessel until the end of the operation, when the latter are delivered free from moisture into the measuring tube.

There are no corks, perforated or otherwise, and but few connections, while the latter are of a character admitting of being secured against leakage. The apparatus while working requires but little attention; so long as the water in the bath is kept boiling, that in the vessel may be regulated efficiently by due adjustment of the mercury cistern.

While this apparatus has rendered me excellent service in extracting the oxygen, nitrogen, and carbonic acid gas dissolved in water, I am of opinion that the *latter* gas, *per se*, can be more satisfactorily estimated by other methods, especially when chalk waters are operated upon, these latter retaining the last traces of free CO_2 with extreme tenacity even after prolonged boiling.

In conclusion, while it is possible that I may have been anticipated in the above contrivance, I feel it to be only fair to state that I am unaware of the fact, and should have been glad of its help long ago.

DISCUSSION.

The Chairman (Mr. Alfred H. Allen) thought Mr. Harvey had added a valuable method to those available for carrying out the troublesome operation of extracting gases from water. By operating under diminished pressure, the great advantage was obtained of securing the ready and complete removal of the gases, and Mr. Harvey had again shown the utility of the nitrometer, the use of which, for such purposes, he (Mr. Allen) was one of the first to advocate.

Mr. H. Droop Richmond asked Mr. Harvey how the free carbon dioxide compared with the combined carbon dioxide; were they equal in quantity, as they should be if the carbon dioxide existed as bi-carbonate? He (Mr. Richmond) had determined the free carbon dioxide, not by actual separate measurement, but by a very obvious method, that of adding an excess of standard baryta and titrating back, using

phenolphthalein as indicator. He had found in certain waters that there was a very considerable deficiency of free carbon dioxide, compared with the quantity that would be theoretically required to form hydro-carbonates. He might mention that in one or two cases the carbon dioxide obtained by the method that he had used had been compared with the actual carbon dioxide obtained by boiling the water, passing the steam through a condenser, absorbing and weighing the carbon dioxide. The combined carbon dioxide he had estimated by the method devised by Mr. Hehner for estimating hardness in water, that is, titrating the water with dilute standard acid, with methyl-orange as indicator.

Mr. Harvey, replying to Mr. Richmond, said that he was first attracted to the question of the accurate estimation of free carbon dioxide by the extraordinary discrepancies between his own results obtained, not by actual gas measurement, but by other methods, and those of other analysts who had previously examined the same samples, inasmuch as he had found 20 cubic inches per gallon in a certain water, and other observers had found 7 or 8. It was very difficult to get the whole of the gas out. Unless by very long boiling it was impossible, and in estimating he had given up the attempt to boil the water in an ordinary flask and at the ordinary pressure. In his opinion, the method he had shown was the only way in which the gas could be got out. By this means he had been able, for the first time, to confirm the results obtained through other processes. In chalk waters he had found the free CO_2 at least equal to the amount in combination with the lime present.

Dr. Teed asked Mr. Harvey if he paid any attention to the presence of sodium carbonate, as certain waters frequently contained that compound.

Mr. Harvey said that he did not find any sodium carbonate existing in such (chalk) waters. The sodium existed in the form of chlorides.

The Chairman said that he had known instances where 7 to 8 grains per gallon of carbonate of calcium had remained dissolved in the water, even after long boiling, provided that evaporation was prevented.

Mr. Harvey observed that in the precipitation of carbonate of lime by Clark's process there was a great deal to learn yet. He had watched the process day by day, and he was in a position to say that there were occasions when the precipitation was instantaneous, but it was within his knowledge that in some cases it was not complete for sixty or seventy hours afterwards.

The two following papers were read by Mr. Moor.

ON THE DETECTION OF EXHAUSTED GINGER.

By A. H. ALLEN AND C. G. MOOR.

SINCE the publication of the paper of Dr. Dyer and Mr. Gilbard in THE ANALYST for August, 1893, purchases of ground ginger under the Sale of Food and Drugs Act have been made in various parts of the country. In order to report on such samples to the best advantage, we have made a series of experiments on various specimens of ginger, and have collected data of considerable interest.

Taking advantage of the experience of Dyer and Gilbard, we have in each case determined the proportion of soluble ash, by which we mean the percentage on the original ginger which is dissolved out on treating the total ash with boiling water. In practice, perfectly good results are obtainable by regarding as the "soluble ash" the difference between the weight of the total ash and the ash insoluble in water. The aqueous solution can, of course, be used for determining the alkalinity, or the actual potash present.

Dyer and Gilbard found the proportion of soluble ash from genuine ginger to vary from 1.9 to 3 per cent., with an average of 2.7, while Mr. W. C. Young found in seven authenticated samples of ginger a range of 1.8 to 2.6 for the soluble ash. Figures for five samples of genuine ginger of unknown origin have been communicated to us by Mr. T. H. Pearmain, and show soluble ash ranging from 1.8 to 2.7 per cent., calculated on the moisture-free samples. The following are Mr. Pearmain's figures:

	1.	2.	3.	4.	5.
Total ash, less sand	3.1	3.9	3.7	5.0	4.5
Ash soluble in hot water	2.2	2.7	2.4	1.8	2.0
Fixed ether extract	3.2	3.0	2.5	5.0	4.2
Alcoholic extract after treatment with ether	2.7	3.1	3.4	2.9	3.0

These results bear out in the main those of Dyer and Gilbard.

Contrary to the general impression, for the manufacture of essence of ginger an aqueous or very dilute alcoholic liquid is employed. The use of any but very dilute spirit, 75° U.P., causes the solution of a considerable quantity of resinous matter, which is precipitated when the essence is subsequently diluted with the water of the ginger-beer. Hence, the use of alcohol in anything more than the most moderate proportion is neither necessary nor desirable, and the more so as the greater part of the pungent and flavouring principle of ginger is readily extracted by cold water. Exhausted ginger having already been subjected to treatment with water or a slightly alcoholic solvent, the soluble portions have been to a great extent removed, and hence such ginger yields a lower extract than a genuine article. The aqueous extract contains a considerable quantity of soluble salts of organic acids, and the ash is correspondingly deficient in soluble salts, and especially in compounds of potassium. In consequence of the presence in ginger of calcium salts soluble in dilute alcohol, the ash left on igniting the proof-spirit extract often considerably exceeds the proportion of soluble ash. This curious fact is no doubt due to the conversion of these calcium compounds into carbonate by ignition, thus rendering them insoluble in water.

In the hope of finding a solvent which would dissolve the valuable portion of the ginger without affecting the objectionable resinous matters, we have examined the action of cold water, proof-spirit, and rectified spirit on a number of samples of ground ginger of commerce. The following results were obtained by Mr. Haywood Court. Sample A was known to be genuine, but most of the others were purchased under the Sale of Food and Drugs Act, and some of them were ultimately admitted to contain an admixture of exhausted ginger.

	A.	B.	C.	D.	E.	F.	G.	H.	I.	J.	K.	L.	M.
Total ash	3.54	5.23	4.41	5.15	5.53	7.69	5.39	3.61	3.19	2.72	3.52	3.29	4.50
Ash soluble in hot water ...	2.36	2.59	2.22	2.57	2.87	2.36	—	1.24	1.45	0.69	1.11	0.97	1.37
Alkalinity of soluble ash as K ₂ O	0.96	0.96	0.29	0.13	0.15	0.20	—	0.27	0.20	0.23	0.23		
Extracted by rectified spirit	7.33	7.70	7.37	6.22	8.45	—	4.65	7.09	—	6.88	7.86		
Extracted by proof spirit {	21.64	20.80	10.70	10.45	7.55	21.60	5.85	13.00	16.08	11.78	12.38		
Containing ash	—	2.73	—	—	—	—	—	2.30	2.47	1.91	2.24		
Extracted by cold water ...	14.57	13.16	14.95	14.55	14.50	14.60	8.14	8.33	9.78	8.51	7.18	8.08	7.39
Extracted by subsequent treatment with proof spirit	9.77	9.59	—	—	—	7.49	—	8.35	8.51	7.76	8.42		
Extracted by subsequent treatment with rectified spirit	1.11	1.28	—	—	—	1.31	—	1.58	0.98	1.28	1.71		
Total extract by three sol- vents used consecutively.	25.45	24.03	—	—	—	23.40	—	18.26	19.27	17.55	17.31		

From these results it appears that the percentage of matter extracted either by proof or rectified spirit affords very little information, the large proportion of resinous matters yielded both by genuine and exhausted ginger masking any minor differences. It is true that Dyer and Gilbard consider that the proportion of matter extracted by alcohol after complete removal of the ethereal extract is a valuable item to the analyst; but as they found it to range from 2.1 to 3.8 per cent., while in the exhausted samples it varied from 0.8 to 1.4 per cent., it is evident that any estimate based on this datum must be of a very rough kind.

On the other hand, the proportion of extractive matter yielded to cold water seemed very encouraging, since the amounts dissolved in most cases followed closely the proportions of soluble ash. The following figures were obtained by Mr. R. Waterhouse by the analysis of genuine ginger of known origin, supplied to us by the kindness of Mr. W. Chattaway, of Apothecaries' Hall.

Origin of Ginger.	N.	O.	P.	Q.	R.	S.	T.	U.	V.	W.	Average.
	Jamaica.	Jamaica.	Jamaica.	Jamaica.	Jamaica.	Cochin.	Cochin.	Cochin.	African.	African.	
Moisture...	11.26	10.98	13.95	12.76	13.96	10.64	13.50	13.23	15.97	13.70	13.00
Total Ash...	—	—	3.90	3.29	3.45	—	3.81	3.62	3.66	3.90	3.66
Soluble Ash	1.70	1.41	3.05	1.75	1.71	1.71	2.03	2.04	2.28	2.41	2.01
Cold-water Extract ..	15.65	13.25	14.40	12.25	11.85	13.00	8.65	11.65	10.80	10.10	12.12

Somewhat closer figures are obtainable by calculating the results on the moisture-free samples, but even then the figures show a good deal wider variation for the soluble ash than was observed by Dyer and Gilbard, while the cold-water extract also shows a wider range than we had expected. Sample *T* presents the peculiarity of yielding the average proportion of soluble ash, but an abnormally low water-extract. On the other hand, sample *O*, which gave the lowest soluble ash, yielded a cold-water extract above the average.

It appears, therefore, that neither the soluble ash nor the cold-water extract affords by itself a perfectly safe means of deciding as to the presence of exhausted

ginger, but by a combination of the two data it is possible to arrive at a more definite conclusion.

More extended observation is needed before anything like a definite limit of composition can be assigned to genuine ginger, and hence it is desirable to leave a wide margin when stating the proportion of exhausted ginger present in a sample. But, meanwhile, there is no difficulty in ascertaining the presence of the adulterant when it has been added in such quantities as to bring the soluble ash down to something like 1 per cent., and the cold-water extract to less than 8 per cent.; and this is the case with not a few gingers in the market. The adulteration has been admitted in several cases of this kind which have come under our notice.

We have pleasure in acknowledging the valuable assistance rendered by Mr. H. Court and Mr. R. Waterhouse in making the experiments above recorded.

DISCUSSION.

Dr. Bernard Dyer said that when he and Mr. Gilbard read their paper before the Society they dealt with Jamaica, Cochin, African and Bengal gingers. They had not at that time come across any samples of Japanese ginger. Since the reading of their paper he had analyzed three samples of Japanese ginger. They gave the following results:

		Approximate essential oil.		Fixed ether extract.		Alcoholic extract after ether.		Total ash (less sand).		Ash soluble in water.
"Japan" ...	...	0.60	...	4.12	...	1.96	...	5.15	...	1.66
"Limed Japan" ...	...	0.68	...	4.14	...	1.74	...	6.58	...	1.74
"Washed split Japan"		0.56	...	4.98	...	3.66	...	3.34	...	1.08

He did not know if Japanese ginger occurred to any extent in commerce.

Mr. Richmond, referring to the soluble ash, said that in the insoluble ash of milk he had observed the presence of a considerable quantity of alkaline salts, which possibly existed as sparingly soluble calcium, sodium, or potassium compounds. Such salts were also found in the ashes of many plants; for instance, he believed that several disputes had occurred with the analysts to the Board of Inland Revenue as to the amount of soluble ash in such things as tobacco and snuff, and in at least one of these cases discrepancies had been traced to the fact that calcium sodium carbonate was present. This was a very troublesome thing to wash out, and it was very hard to say when the operation was completely performed. He thought it probable that a small excess of calcium salts in ginger might keep back some of the soluble ash. In reality, determination of soluble ash was not a very accurate determination, and possibly, if, instead of estimating the soluble ash, the actual amount of alkaline base were estimated, more concordant figures would be the result.

Dr. Walter J. Sykes asked if the method of extracting and estimating the essential oil of ginger by means of petroleum ether, proposed by Dragendorff as a general method for the separation of essential oils from resins, had been tried. In the vast majority of substances the volatile oil of the plant-derivative was soluble in petroleum ether, and the resin insoluble.

Mr. W. Chattaway said that Japanese ginger was a thing almost unknown in the trade, so far as any large sale was concerned. He did not believe that split ginger

(which he had never met with) was used in commerce to any extent. He confirmed what Dr. Sykes had said respecting the direction in which it seemed most desirable to work in connection with the detection of exhausted ginger. The volatile oil figure in a sample of ginger would suffer from washing. A considerable quantity could be removed with cold water.

Mr. Allen said that it had been clearly shown that they were again dealing with one of those natural products which varied very materially in composition. Milk was supposed to be strictly a natural product, but in the case of ginger the substance was subjected to a certain treatment. He had become aware that it was usual to dip the ginger into boiling water as a preliminary stage in manufacture, and if it was dipped a little too much, or previously split, it was possible that more might be dissolved than analysts anticipated. It might be imagined that there was a sort of film of gelatinous starch formed on the outside of the root, and it would be difficult for the water to dissolve matter from the interior. They had tried to find some datum by which ginger could be judged. The aromatic principle of ginger was easily soluble in water, and although if ginger were soaked in water the flavour was not wholly removed, still a very great part of it went into the cold water, and it was only necessary to evaporate the water to discover that such was the case. It was highly probable, as suggested by Dr. Sykes, that it would be capable of being dissolved out by petroleum spirit, and might perhaps be extracted from its aqueous solution by agitation with that solvent. As to the estimation of actual alkalies mentioned by Mr. Richmond, it would be found in one of the tables that they did estimate the alkalinity of the soluble ash, and had expressed the results in terms of potash. He believed it was a fact that Mr. Stock estimated the potash as chloroplatinate, which seemed very desirable in certain cases. Although at present there was no single satisfactory datum on which to judge ginger, by a careful consideration of the results yielded by several methods of treatment it was possible to arrive at a very fair approximation to the truth. The descriptions of ginger referred to by Dr. Dyer were mere curiosities of no commercial interest, and hence the abnormal results yielded by them did not affect the practical value of the deductions from the proportion of soluble ash and other data. It was also an interesting fact that the gingers of low soluble ash had recently almost entirely disappeared from districts where prosecutions had been instituted.

ON THE CHANGE IN THE COMPOSITION OF BUTTER BY LONG KEEPING.

BY A. H. ALLEN AND C. G. MOOR.

IN the discussion on a paper recently read before this Society by Mr. Richmond, a question arose as to the extent to which butter decomposed by long keeping. As a contribution to the existing knowledge on this obscure question, it occurred to us that it would be interesting to analyze some samples of butter which had been in our possession since November, 1888. These samples were closely packed in tins, and had remained intact since the packages were sealed in Denmark more than five

years ago. The butter-fat obtained by rendering the fresh butter was analyzed at the time very carefully, and the results were published in a paper by one of us in *THE ANALYST* for January, 1889.

Three tins of the "B" butter and one of the "O" butter still existed, and it is the fat from these which we have recently submitted to analysis. The samples of "B" were badly decomposed, but the one remaining portion of "O" showed little or no sign of decomposition. It will be observed that the change undergone by this butter, as indicated by the results of the analysis, is comparatively trifling, whereas in the samples of "B," in which the decomposition was much more profound, the changes are extreme. Further, the changes in portions "B 1," "B 2," and "B 3," which have been kept side by side since 1888, have not proceeded with the same rapidity.

We are pleased to acknowledge the zealous assistance of Mr. G. S. A. Caines, who made the recent analyses given in the following table :

	Butter marked "B."					Butter marked "O."		
	Rendered and Analyzed November, 1888.		Rendered and Analyzed March, 1894.			Rendered and Analyzed Nov., 1888.	Rendered and Analyzed Nov., 1888.	Rendered and Analyzed March, 1894.
	<i>Copenhagen.</i>	<i>London.</i>	<i>London.</i> 1	<i>London.</i> 2	<i>London.</i> 3	<i>Copenhagen.</i>	<i>London.</i>	<i>London.</i>
Specific gravity at 100° C. ...	·8639	·8640	·8634	·8696	·8730	·8641	·8641	
C.C. of $\frac{N}{10}$ alkali required for 5 grammes by Reichert-Wollny process ...	22·63	22·39	14·43	12·02	12·02	24·39	24·70	22·48
Percentage of KHO required for saponification ...	22·27	22·05	21·99	22·55	22·88	22·15	22·03	23·33
= Saponification equivalent ...	251·9	254·4	255·1	248·7	245·2	253·3	254·6	240·4
Soluble fatty acids, per cent. ...	—	$\begin{cases} 4·37 \\ 4·50 \\ 4·45 \end{cases}$	3·82	5·66	5·80	—	$\begin{cases} 4·60 \\ 4·66 \\ 4·77 \end{cases}$	5·89
Insoluble fatty acids, per cent. ...	—	$\begin{cases} 90·24 \\ 90·62 \end{cases}$	90·73	90·70	90·00	—	$\begin{cases} 89·90 \\ 90·30 \end{cases}$	85·78
Iodine absorption, } per cent. ...	Not done	Not done	30·01	27·17	25·08	Not done	Not done	25·57
Condition of the butter when rendered ...	Fresh	Fresh	Decomposed	Decomposed	Decomposed	Fresh	Fresh	Showed no signs of decomposition.

DISCUSSION.

Mr. Allen said that the figures were no doubt surprising, and he could not see his way to offer any definite explanation of them. It would be noticed how, in the

samples of "B" recently analyzed, the Reichert figure had fallen from 22 to 14, and even to 12, whereas in the sample marked "O" it had fallen from 24.7 to 22½. On the other hand, if the figures for the soluble acids were examined, it would be found that, out of three tins of the same butter kept side by side, only one had undergone decrease. The insoluble acids had not very greatly altered. The iodine absorption also varied. The figures seemed to indicate that it was impossible to tell from such data—without going into the differentiation of the nature of the volatile acids—what change had occurred; nor could it be said that, because one sample of butter had altered in a certain manner, another was likely to alter in the same way. The two samples "B" and "O" had behaved in a different manner, though they had been kept under the same conditions as to exposure, absence of light, etc. It was not very often that an opportunity presented itself of making analysis of butter after so long a period of time.

Dr. Sykes thought it possible that the differences observed on long keeping might be explained by the differing nature of the bacteria which had obtained access to the samples. So far as he knew, the effects of bacterial action upon fats had yet to be worked out.

Mr. Richmond said that, in the butters which had decomposed, the disturbance between the normal ratios of the figures determined was very marked. It would be noticed in the three samples "B" that the Reichert-Wollny figure had gone down very considerably. The figure for the soluble fatty acids had, in the first case, gone down a very little, but by no means in proportion to the volatile acids, and in the other two it had gone up. When butter decomposed a hydrolysis undoubtedly took place, and the liberated fatty acids would be partly dissolved in the water of the butter. The same order of things was apparent in the case of the butter "O" as in "B," although the Reichert-Wollny figure had not gone down to such a marked extent. The figure for the soluble fatty acids had, however, gone up. About two years ago he had occasion to make determinations on about fifteen or sixteen samples, and estimating the Reichert-Wollny figure and the soluble acids, he found that the relations between the two were fairly constant. A mean ratio of 86.5 per cent. was found in the distillate, and this agreed fairly with the ratios originally found by Mr. Allen. In the examples shown on the board it was very easy to see that the ratio of the quantity distilled over in the Reichert-Wollny process to the total soluble acid had gone down to something like 50 per cent. in the butter marked "B 1," and about 70 per cent. in the butters marked "B 2 and B 3." There was also a change in the iodine absorption. When the butters were analyzed in 1888 iodine absorptions were not determined. Working in Mr. Hehner's laboratory, he had also, through the kindness of Mr. Allen, examined these butters; he believed his Reichert-Wollny figure was almost the same; as far as his recollection went, the iodine absorption was close upon 40 per cent.; so taking this as the original figure, there had evidently been a large diminution. As regarded the increase in the soluble fatty acids, it was evident that they were not distilled over in the Reichert-Wollny process, and, therefore, that they could not be the same kind of acid as that distilled, that is to say, the lower fatty acids of the acetic acid series. Some years ago a series of papers was

published by Hazura, who studied the action of alkaline permanganate, and he obtained by oxidation hydroxyacids from the unsaturated fatty acids of various kinds. Some of these acids were soluble in water, and he (Mr. Richmond) thought it was highly probable that old butters would contain considerable percentages of hydroxyacids produced by oxidation. Hydroxyacids had a high density, and the increase of density again indicated the presence of this class of compound. He had in his possession a sample which had been sealed up by Dr. Vieth, and which had been kept for a considerable time; the air had been excluded from it, it had been kept in the dark, and it showed no signs of decomposition. It would seem that if the butter was excluded from the air it kept much better, and that oxidation was an important factor. This was one of the facts which led him to think that the soluble acids might be hydroxyacids soluble in water. From a study of the results of fractional distillation of butter acids he had evidence of a soluble acid of less volatility than butyric, and it was not impossible that this was a hydroxyacid (*e.g.*, lactic). He would like to mention that it was extremely useful to determine the rise of temperature with strong sulphuric acid. He had found in the case of olive-oil that the rise had a quantitative meaning, and that a certain amount of rise could be assigned to acids of each series. It would be extremely interesting to determine it if the authors had a sufficient quantity of the butters left. He (Mr. Richmond) had given up the use of 50 grammes of the oil or fat for 25 grammes oil and 5 c.c. of acid, and found the results more accurate. In fact, he found that, with the apparatus which he used, he could get within 1 or 2 tenths of a degree centigrade. Messrs. Allen and Moor's figures were of great interest, and there seemed considerable hope that the analysis of decomposed butter would afford information as to its original composition. Glycerol determinations might be of use, as probably this would be attacked.

Mr. Moor stated that in the case of the "B" butters the samples had attacked the tinned iron box, and were quite brown in colour; whereas this was not the case with the "O" butter, which did not show any appearance of decomposition, or possess the strong smell of bad cheese which characterized the "B" samples.

In the absence of the author, the following paper was read by Dr. Dyer :

CESHIRE CHEESE.

BY CHARLES M. BLADES.

The cheese produced by the farmers of Cheshire at one time held the highest reputation of any obtained from the other counties in England, both for richness in flavour and in butter fat. This important article of food has, however, sadly deteriorated in quality, not through the loss of the art or skill in the manufacture, as it has frequently been asserted, or through the richness of the pastures declining, but through that pernicious habit of retaining a portion of the cream from the milk for butter making. By some the night's milk is skimmed, and the skimmed milk added to the morning milk to be converted into cheese, while the cream removed is made into butter. Others adopt the more scientific method of half milking the cows, and keep the first portion separate to be converted into cheese; the cows are then milked dry, and the latter portion used for making butter.

Much care and scientific attention have been devoted to check the skimming and watering of milk; surely the almost equally important article of food—cheese, which forms the staple diet of a very large portion of our population, demands more attention than it has hitherto received by the inspectors under the Food and Drugs Acts.

The following analyses represent samples obtained from respectable retailers, only one of which indicates whole-milk cheese:

	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.
Water ...	52·60	44·00	42·90	36·10	49·87	42·06
Fat ...	9·85	26·12	20·02	30·67	20·82	21·84
Casein, etc....	32·95	25·08	32·58	28·23	24·44	32·20
Ash ...	4·60	4·80	4·50	5·00	4·87	3·90
	100·00	100·00	100·00	100·00	100·00	100·00

DISCUSSION.

Mr. Allen thought that the results obtained by Mr. Blades were very curious. The amount of water struck him as being excessive. He did not think he had seen cheese with more than 35 or 40 per cent. of water. He would like to know how far Mr. Blades succeeded in completely extracting the fat from the cheese. Under ordinary circumstances he (Mr. Allen) had not troubled to get all the fat out. A convenient way was to grind up the cheese with sand prior to extraction. It was open to question whether Mr. Blades had succeeded in extracting the whole of the fat, and if he had not been successful in doing that it would modify the result.

Mr. Richmond, referring to the question of the estimation of the fat, said that there was a method used by the American Association of Official Agricultural Analysts for the estimation of fat in cheese, which consisted in weighing out a portion of the cheese and grinding it up with twice its weight of anhydrous cupric sulphate, which absorbed the whole of the water, and the fat was comparatively easily extracted. From the results reported by them the method seemed to give exceedingly concordant results. He wished to know whether any information had been given in the paper as to how the casein was estimated. He presumed it was either estimated by determining the total nitrogen and multiplying by a factor, or by a subtraction of the weight of the water, fat and ash. Either method would give too high results for casein. Personally, he held the view that there was no casein in cheese. The albuminoid matter in cheese was the product of the action of rennet, and it contained a sensibly smaller proportion of nitrogen than casein. Casein contained about 15·7 per cent. of nitrogen, while the albuminoid matter of cheese contained about 14·3 per cent. In estimating the casein or the albuminoid matter of cheese by the estimation of nitrogen it was necessary to multiply by a higher factor than 6·25 or 6·33, or 6·38, which were the factors generally used. In the ripening of cheese there was a considerable amount of decomposition of the albuminoid matter. Small quantities of amido-compounds, and even ammonia, were found, and, in estimating the nitrogen of cheese, those ought to be taken into account. He thought that the only way of actually estimating the albuminoid matter of cheese was to form an insoluble

albuminoid compound by means of acetate of lead, or by Stutzer's method, and wash the other compounds out, estimating the nitrogen, and assuming that there was 14.3 or so in the cheese. In making cheese, when the milk was submitted to the action of rennet, the whole of the albuminoids were not contained in the cheese obtained—there was a considerable percentage in the whey. If it was assumed that milk contained 3.4 per cent. of albuminoid matter, the amount which went into the cheese was about 2.7 per cent. The greater portion of the fat was taken down, too; but there was also some fat left in the whey. He thought the average left was nearly 1 per cent., though this varied considerably. In his experience of the last year, the exceptional weather which had prevailed had had more effect on the quality of Cheshire milk than it had on the quality of the other milks which he had examined. It was true these milks came from half a dozen farms, and he could not say that the samples were strictly authenticated in the legal sense, but there were peculiar circumstances about them which led him to think that the milks had not been adulterated. If his experience were true for the whole of the county, it would account for the fact that the quality of Cheshire cheese was not as good as it has been. The proportions of fat to casein, 26 to 25, 31 to 28, 21 to 24, and possibly even 21 to 32 (that is, after making some allowance for the way in which the casein was estimated) were not so extremely low in fat considering the poor quality of the milk in the district during the past season. With regard to the first one, which only contained 10 of fat to 37 of casein, he thought that was distinctly low, and there was not any doubt at all that it was a cheese made from skimmed milk. The third and fifth might also be partially made from separated milk; but as for the others, he thought they were all of them within the limits of the results which would be obtained from the analysis of cheese made from poor milk. He could not agree that the analysis of the cheeses given by the author showed distinct evidence of a general skimming of the milk, and, from what he knew of Cheshire farmers, thought that the falling off in the quality of the cheese was due to the milk having been exceptionally poor.

NOTE ON THE ANALYSIS OF PHOSPHOR TIN.

By FRANK L. TEED, D.Sc.

(Read at the Meeting, April 4, 1894.)

The ordinary method of analyzing this substance is by acting on it with nitric acid, evaporating to dryness, fusing with alkaline carbonates, and extracting the fused mass. Another method is to fuse the finely-divided substance with a mixture of alkaline carbonates and nitrates, and extract the fused mass.

Both these methods have the objection of a fusion being necessary, and in all accurate work a fusion should be avoided if possible. The method I venture to recommend is to oxidize with nitric acid, destroy the excess of nitric acid with ammonium chloride, make alkaline with ammonia, and then warm with excess of ammonium sulphide until complete solution of the tin. Any traces of metals whose sulphides are insoluble in ammonium sulphide are here left undissolved, and may be filtered off.

On acidifying this ammonium sulphide solution the Stannic sulphide is precipitated, and the phosphorus is estimated in the filtrate by addition of ammonia and "magnesia mixture."

DISCUSSION.

Dr. Bernard Dyer said that in the analysis of phosphor tin, he had not been successful in separating the tin and the phosphoric acid in the way that Dr. Teed had suggested, although he had tried it. He found that the phosphoric acid was retained by the tin when the latter was precipitated as sulphide, despite the acidity of the solution. It was an exceedingly difficult thing to separate tin and phosphoric acid. He thought the most accurate way to determine the phosphorus in phosphor tin was the following: First attack the metal with nitric acid, subsequently add hydrochloric acid, and thus get all the phosphorus into the state of phosphoric acid and the tin into solution. The hydrochloric acid should be present in as small a quantity as possible, only just enough to ensure the metal being kept in solution. This was important. Then the phosphoric acid could be determined in the usual way by means of molybdenum. Of course it was easy to dissolve the phosphor tin in hydrochloric acid at once, but that involved a wholesale loss of phosphorus in the form of hydrogen phosphide. He had tried Dr. Teed's method—or, rather, the similar method laid down in Fresenius—some two or three years ago, and though he made several attempts, he could not make it work satisfactorily.

Mr. Hehner said he would like to know how Dr. Dyer had treated his precipitate. The precipitate should consist of oxide of tin.

Dr. Teed inquired if Dr. Dyer had been very careful in getting rid of his nitric acid; if that were not properly effected the phosphoric acid must go down.

Dr. Dyer said it was some time since he performed the experiments, and he could not remember the details; but he followed those laid down by Fresenius, and was quite disappointed with the result.

NOTE ON LEMON AND ORANGE PEEL.

By E. G. CLAYTON.

(Read at the Meeting, April 4, 1894.)

When orange-peel is moistened with strong hydrochloric acid, its colour changes from yellow to a rich dark green; lemon-rind, similarly treated, retains its hue, or, at most, assumes a dingy, yellowish-brown tint. A convenient and simple chemical test, therefore, which will distinguish between small fragments of lemon and orange peel is to touch them with a glass rod previously dipped in hydrochloric acid. The diluted acid will answer the purpose, but the reaction is slower.

A few minutes' exposure to hydrochloric acid gas will effect this change in the pigment of orange-peel. The colour of lemon-rind is unaffected.

The shades of green developed by dilute hydrochloric acid are deepest in the cases of Mercia, Denia, and Florida oranges; of moderate intensity with Jaffa and

“ blood ” oranges ; and feeble with Valencia and Tangerine oranges. This statement also applies to the reactions with *strong* hydrochloric acid, excepting that the colour of Tangerine orange-peel with the strong acid is perhaps more intense than that observed with any of the other varieties of the fruit.

The peel of the lime behaves, with hydrochloric acid, like lemon-rind.

Mr. Hehner remarked that it was not at all an infrequent occurrence for lemon and other peels to be artificially coloured. He thought that at present too implicit reliance should not be placed on this test in the case of candied-peel.

The Determination of Phosphoric Acid by the Titration of the Yellow Precipitate with Standard Alkali. H. Pemberton, Jur. (*Jour. Am. Chem. Soc.*, 1893, 382.)—In a paper read in 1882 the author called attention to the satisfactory results yielded by this method, but it is only recently that he has been able to work the subject out. Since 1882 several chemists have proposed processes based on the same principle, their names and a short description of each modification being given.

In the author's process the following solutions are employed :

Ammonium Molybdate.—Ninety grammes of the crystals are dissolved (in a large beaker) in somewhat less than one litre of water. This is allowed to settle overnight, and the clear liquor decanted into a litre flask. The small quantity of insoluble molybdic acid, always present, is dissolved in a little ammonia and added to the main solution. Should the molybdate be found to contain traces of P_2O_5 , a few decigrammes of magnesium sulphate are added, ammonia being added to faint alkalinity. The whole is then made up to one litre. It is this *aqueous* solution that is used, *no nitric acid whatever being employed*. Each c.c. precipitates 3 milligrammes of P_2O_5 .

The *ammonium nitrate* solution is simply a saturated aqueous solution of the salt. Distilled water is poured into the bottle of crystals in quantity insufficient to dissolve them all. Even in cold weather 10 c.c. of this solution is amply sufficient for each test.

The *nitric acid*, used for acidifying the solution of the phosphate, has a specific gravity of 1.4 or thereabouts.

The *standard potassium hydroxide* solution is of such strength that 1 c.c. = 1 mgm. P_2O_5 . One hundred c.c. of it will neutralize 32.65 c.c. of normal acid. It can be made from normal potassium hydroxide (that has been freed from all carbonate by barium hydroxide) by diluting 326.5 c.c. (see next paragraph) to 1 litre. But its strength is best determined empirically by a direct test upon a phosphate solution of known strength, precipitating with ammonium molybdate, and making the analysis as described below, all potassium carbonate having first been removed by barium hydroxide.

In a subsequent paper (*Jour. Am. Chem. Soc.*, 1894, 278), the author gives the details of a number of experiments which he had made, proving that 23 molecules of NaHO are required to neutralize the yellow precipitate containing 1 molecule of

P_2O_5 , and not 23.2 as his previous experiments had led him to conclude. Consequently, the above-mentioned *standard potassium hydroxide* solution should be made by diluting 323.7 c.c. normal solution to a litre instead of 326.5 c.c.

The *standard acid* has the same strength, volume for volume, as the potassium hydroxide, and can be made by diluting 323.7 c.c. of normal acid to 1 litre. In testing it against the alkali, phenolphthalein (and methyl orange) should be used.

The *indicator* can be either litmus, rosolic acid, or phenolphthalein. I have used the latter almost exclusively, as it has been shown by J. H. Long (*Am. Chem. J.*, xi., 84) that titrations with this indicator in the presence of ammonium salts are perfectly reliable if the amount of the ammonium salt present is not excessive, if the solution is cold, and if the phenolphthalein is used in sufficient quantity. One gramme of the phenolphthalein is accordingly dissolved in 100 c.c. of 60 per cent. alcohol, and, at least, 0.5 c.c. of this solution is used for each titration. The washing of the ammonium phospho-molybdate is done by water. (Isbert and Stutzer, *Ztschr. anal. Chem.*, xxvi., 584, have shown that there is no danger of loss in washing the yellow precipitate with water.)

The following is the method of performing the analysis :

One gramme of the phosphate is dissolved in nitric acid, an excess of which can be used with impunity, and the solution filtered into a 250 c.c. flask and made up to the mark. The solution can even be poured into the flask without filtering, since the presence of a little insoluble matter does not interfere in the least with the titration. Moreover, since most phosphate rocks seldom contain over 10 per cent. of insoluble matter, and as this has the specific gravity of, at least, 2, it occupies a volume of about 0.05 c.c., an amount so small that it may be neglected. (For instance, even in the case of a phosphate rock containing 40 per cent. P_2O_5 , the error is only 0.008 per cent. P_2O_5 .)

After the clear solution has been poured off, it is well to treat the sand, etc., at the bottom of the beaker, with a c.c. or so of hydrochloric acid, in the warmth, to insure complete solution.

It is not necessary to evaporate to dryness. Isbert and Stutzer have shown in their paper that when the yellow precipitate is washed with water, the soluble silica is removed, and that evaporation (to render the silica insoluble) is superfluous. Their results have been corroborated by test analyses. In the event of its being desirable to remove silica by evaporation for any purpose, the evaporation should be performed over a water-bath, or, if on an iron plate, with great care, since, otherwise, meta- or pyro-phosphates are formed, with results that are correspondingly low.

Twenty-five c.c. of the solution (equal to 0.1 gramme) are now measured out and delivered into a beaker holding not more than 100 to 125 c.c. A large beaker requires unnecessary washing to remove the free acid in washing the yellow precipitate. The solution is neutralized with ammonia—until a precipitate just begins to form—and 5 c.c. of nitric acid of sp. gr. 1.4 added; 10 c.c. of the ammonium nitrate solution are added, and the entire bulk of the solution made up to 50 to 75 c.c. by adding water.

Heat is now applied, and the solution brought to a full boil. It is then removed from the lamp, no more heat being applied, and treated *at once* with 5 c.c. of the

aqueous solution of ammonium molybdate, which is run into it from a 5 c.c. volume pipette, the solution being stirred as the precipitate is added. The beaker is now allowed to rest quietly for about one minute, during which time the precipitate settles almost completely. The 5 c.c. pipette is filled with the molybdate solution, and a part of its contents allowed to drop in, holding the beaker up to the light. If a formation of a yellow cloud takes place—it is at once perceptible—in which case the remainder of the pipetteful is run in, the solution stirred and allowed to settle. A third pipetteful is now added as before. Should it cause no further cloud, only about one-half of its contents is added, the remainder being run into the beaker into which the filtrate and washings from the yellow precipitate are to go. In test analyses it was shown that, even when 15 c.c. in excess of the molybdate were purposely used over and above the calculated amount, the results were accurate, no molybdic acid coming down with the yellow precipitate.

It is seldom that more than 15 c.c. in all (three 5 c.c. pipettefuls) of the molybdate have to be added. Since each c.c. precipitates 3 milligrammes P_2O_5 , 15 c.c. will precipitate 45 milligrammes P_2O_5 . This is equivalent to 45 per cent. on the 0.1 gramme taken for analysis, and it is not often that any material to be examined contains over this percentage. In the analysis of materials rich in phosphoric acid, it is one of the embarrassing features of the usual process, in which the *nitric acid solution* of the molybdate is used, that, in the first place, large quantities of the precipitant have to be used (frequently several hundred c.c.), and in the second place, that the analyst is never certain that enough has been added to throw down all of the phosphoric acid. This necessitates frequent testings of small portions of the phosphate solution or of the filtrate. There is another difficulty peculiar to the process as usually carried out in all methods in which the determination is made directly upon the phospho-molybdate itself, in that much care must be observed to keep the solution at a certain temperature, since otherwise molybdic acid contaminates the precipitate and the analysis is rendered worthless. In the process herein described, using an *aqueous* solution of the molybdate, the point at which sufficient of the precipitant has been added is easily seen. No molybdic acid separates, because, in the first place, no great excess of molybdate is added; and because, in the second place, the solution is filtered immediately, or as soon as it has settled, which requires only a minute or two. The time required from the first addition of the molybdate to the beginning of the filtration is never over ten minutes, and is generally less. The filtrate and washings from the precipitate when treated with additional molybdate solution, give, on standing on a hot plate for an hour or so, a snow-white precipitate of molybdic acid, showing that all of the phosphoric acid has been precipitated.

A slight correction should be made to the statement made above in regard to 15 c.c. of the molybdate precipitating 45 milligrammes of P_2O_5 . This is not strictly true, for the reason that a small quantity (something over 1 c.c.) of the molybdate is required to neutralize the solvent action of the nitric acid. Therefore, in *very* high grade phosphates a fourth 5 c.c. pipetteful may be required.

The yellow precipitate is now filtered through a filter 7 centimetres in diameter, decanting the clear solution only. This is repeated three or four times, washing

down the sides of the beaker, stirring up the precipitate, and washing the filter and sides of the funnel above the filter each time. The precipitate is then transferred to the filter and washed there. When the precipitate is large it cannot be churned up by the wash water, and cannot be washed down to the apex of the filter. This is generally the case when there is over 10 or 15 per cent. phosphoric acid present in the substance analyzed. In such an event, the precipitate is washed back into the beaker, and the funnel filled with water above the level of the filter, this being done two or three times, then the precipitate washed back into the filter. It is not necessary to transfer to the filter the precipitate adhering to the sides of the beaker.

It goes without saying that during the washing no ammonia must be present in the atmosphere of the laboratory. Inasmuch as the beaker, funnel, filter and precipitate are small, the washing does not take long to perform. It requires, in fact, from ten to fifteen minutes, even when large precipitates ($= 30$ to 40 per cent. P_2O_5) are handled. The precipitate and filter are now transferred together to the beaker. The alkali solution is run in until the precipitate has dissolved, at least twelve drops of the phenolphthalein ($1 : 100$) are then added, and the acid run in without delay until the pearly colour disappears and the solution is colourless. The presence of the filter paper does not interfere in the least. The reaction of the indicator is not so sharp as when only acid and alkali are used, but it is easy to tell with certainty the difference caused by one drop of either acid or alkali. After deducting the volume of acid used from that of the alkali, the remainder gives the percentage of P_2O_5 directly, each c.c. being equal to 1 per cent. P_2O_5 . Thus, if there are 28.3 c.c. of alkali consumed, the material contains 28.3 per cent. P_2O_5 when one decigramme is taken for analysis. From the time the 25 c.c. are measured out until the result is obtained, from thirty to forty minutes are required.

The author has applied this process to determinations of phosphoric acid in phosphates and fertilizers, but has had no experience in determining phosphorus in iron, steel, or iron ores. He is inclined to believe that in the presence of such large quantities of iron salts, when using the *aqueous* solution of the molybdate, it may be necessary to guard against contamination of the yellow precipitate by ferric hydrate, perhaps by using larger quantities of nitric acid than 5 c.c., and perhaps by washing the precipitate at first with dilute nitric acid. It may also be the case that the yellow precipitate will form more slowly.

Test analyses gave satisfactory results.

W. J. S.

The Volumetric Estimation of Sulphuric Acid. W. Windisch. (*Wochenschrift f. Brauerei*, 1894, p. 607.) This method depends upon the precipitation of the sulphuric acid by an excess of barium chloride solution of known strength; the excess of barium is next removed by an excess of potassium chromate solution (also of known strength), and then the excess of chromate quantitatively determined. Several methods were tried for the last determination, first oxalic acid, then ferrous salts, both of which were rejected, since it was found that the former acted irregularly, and that it was difficult to secure stable solutions of the latter. Arsenious acid, which acts according to the following equation, $4CrO_3 + 3As_2O_3 = 2Cr_2O_3 + 3As_2O_5$, proved a

reliable agent for this purpose, and it was shown that the reaction was the same either in an acid or an alkaline medium.

The following decinormal solutions are required: (1) Solution of barium chloride, containing 23·386 grammes of the salt per litre; (2) potassium chromate solution, with 19·4561 grammes per litre; (3) arsenious acid solution, with 4·95 grammes As_2O_3 per litre; (4) iodine solution, containing 12·7 grammes per litre. The arsenious acid, which must be perfectly pure, is dissolved in a small quantity of warm NaOH solution, and then sulphuric acid added to slight acid reaction.

In the actual determination $\frac{N}{50}$ solutions, prepared by diluting the above, are made, and these are titrated the one against the other, in order to ensure absolutely accurate relations between them.

For the estimation of the sulphuric acid in a water, 100 c.c. of it are taken; or, in the case of waters containing small quantities of sulphates, several 100 c.c. are evaporated to 100 c.c., with the addition of a little HCl, the water being subsequently neutralized, or made slightly alkaline with ammonia. The water is brought to the boil, 50 c.c. of the $\frac{N}{50}$ barium chloride added, and immediately afterwards an equal quantity of the $\frac{N}{50}$ potassium chromate solution. After being boiled for one or two minutes, the whole is brought into a 300 c.c. flask, cooled and made up to 300 c.c. Portions of 100 c.c. each are now filtered off, and to each of these 50 c.c. of the $\frac{N}{50}$ arsenious acid solution and 5 c.c. of 20 per cent. H_2SO_4 added, well shaken, and allowed to stand until the solution has become colourless: this takes place in two or three minutes. Should the first 50 c.c. not be sufficient to decolorize the mixture, a second similar quantity is added. A little starch solution is then added, also a small quantity of a cold saturated solution of hydric sodium carbonate, and the liquid titrated with the $\frac{N}{50}$ iodine solution, until a permanent pale-blue colour is produced. If T equals the titre between the iodine and arsenious acid solutions, T_2 that between the arsenious acid and potassium chromate solutions, and I the number of c.c.'s of iodine solution used, then: $x = \frac{12(T_1 - I)}{T_1 \times T_2}$ grammes of sulphuric anhydride (SO_3) in the quantity of the water taken.

A number of examples are given showing that the process gives results which are in the most satisfactory concordance with those of the ordinary gravimetric process, both in the estimation of the H_2SO_4 in waters and also in sulphates. In estimating the H_2SO_4 in the sulphates of the heavy metals, the metallic oxide is first removed by NH_3 , the solution being afterwards neutralized with HCl. Raw gypsum is first fused with dry sodium carbonate, the melt dissolved in dilute HCl, and exactly neutralized with NH_3 .

W. J. S.

The Tannin-Bodies in Hops, and their Estimation. M. Hayduck. (*Wochens. f. Brauerei*, 1894, p. 409.) The author has prepared samples of hop-tannin and of hop-phlobaphene by Etti's method (*Annalen d. Chemie*, 1876, vol. clxxx.). He describes the pure hop-tannin as being a bright-brown amorphous powder, soluble in water, acetic ether and dilute alcohol; very slightly soluble in absolute alcohol, and insoluble in ether. The 0·2 per cent. aqueous solution has a pale-yellow colour, and shows a greenish fluorescence. Its taste is at first slightly bitter, afterwards astringent.

gent, though not unpleasantly so. Fe_2Cl_6 produces an intense green coloration, but no precipitate; and this forms an exceedingly sensitive test for the presence of hop-tannin. In accordance with Etti's statements, Hayduck found that hop-tannin is precipitated by albumin, but not by gelatin; but, contrary to Etti's statement, it was found to be precipitated by animal membrane. Hop-tannin is acid to litmus; it is decomposed with remarkable ease, simple evaporation in aqueous solution being sufficient to partially convert it into a substance insoluble in water, a small portion being also transformed into phlobaphene. Its complete conversion into phlobaphene is readily effected by the agency of alkalies. If a solution of the tannin be made alkaline with sodium carbonate and evaporated, complete conversion ensues; the same also happens if the tannin be heated in the dry condition to 140°C .

The phlobaphene is a reddish-brown powder, partly soluble in boiling water or dilute alcohol. Its aqueous solution has a yellowish-brown colour, a disagreeable bitter, astringent taste, and gives a dirty dark-green precipitate with Fe_2Cl_6 ; it is precipitated by albumin, and is also removed from its aqueous solution by hide. The larger portion of the phlobaphene obtained is insoluble in water, but dissolves in alkaline solutions with a deep-brown colour, from whence it is reprecipitated by acids. The soluble form shows a great tendency to pass into the insoluble one, simple boiling in water, or heating the dry substance to 130°C ., effecting this change.

After reviewing the various methods which have been proposed from time to time for the estimation of the tannin-bodies in hops, Hayduck concludes that Lowenthal's method is the most reliable one, and proposes the following procedure: The hops are first extracted with ether to remove hop-resin, dried, and coarsely powdered in a coffee-mill. Ten grammes of the hops so prepared are extracted by boiling with six successive portions of distilled water of 100 c.c. each. The first boiling lasts an hour, the subsequent ones half an hour each. The extracts so obtained are mixed and made up to 500 c.c., cooled and filtered. An apparatus designed by Prof. von Schröder is strongly recommended for the extraction. It consists of a cylindrical vessel of tin-plate, provided with a spout, into which fits fairly tightly a perforated plate, furnished with a handle. The perforated plate is covered with fine gauze, and after each boiling the plate is gently pressed down towards the bottom of the vessel; the solid matter is retained by the strainer; the extract passes through the gauze. To remove the hop-tannin-bodies from the portion of the solution required for the second titration, 5 grammes of powdered hide are soaked in water for twenty-four hours, squeezed as dry as possible in a linen cloth, and added to 100 c.c. of the hop-extract, then allowed to remain for twenty-four hours, the mixture being occasionally well shaken. The quantity of water taken up by the powdered hide is estimated and allowed for subsequently.

For the actual determination 10 c.c. of the original hop-extract and 10 c.c. of indigo solution are taken, diluted with water to 750 c.c., and titrated with permanganate in the usual manner. The same quantity of the extract after treatment with the hide powder is similarly titrated. The following are the results of such a determination:

Titre of permanganate, 1 c.c. = 0.002026 gramme tannin.

Permanganate required to decolorize 10 c.c. indigo solution = 9.4 c.c.

The 5 grammes of powdered hide had absorbed 11 grammes of water.

The hops contained 9.92 per cent. moisture.

Titration of 10 c.c. of original hop-extract = 12.35 c.c.

Titration of 10 c.c. of hop-extract after treatment with powdered hide = 10.05 c.c.

Deducting from each of these figures the 9.4 c.c. used for decolorizing the indigo, leaves 2.95 c.c. and 0.65 c.c. respectively; and this latter figure, after allowing for the water absorbed by the hide-powder, becomes 0.72. Then $2.95 \text{ c.c.} - 0.72 \text{ c.c.} = 2.23 \text{ c.c.}$ permanganate used by the tannin-bodies, which is equivalent to 2.258 per cent. tannin-bodies in the original hops, or 2.50 per cent. in the water-free hops.

The results obtained in comparative experiments, made with hops before and after treatment with ether, showed very small differences; they were slightly higher (about 0.25 per cent.) in hops without previous treatment. The author considers that it is a difficult matter to decide which of the two is the more correct figure. He has ascertained that the presence of hop-resin in the solution does not make any appreciable difference in the result, and conjectures that the treatment with boiling ether in the extraction apparatus may cause a portion of the tannin-bodies to become converted into the insoluble form.

Some very valuable observations on the part played by hops in brewing conclude the paper.

W. J. S.

A New Method of Analyzing Fats and Resins. Parker C. McIlhiney. (*Jour. Am. Chem. Soc.*, 1894, p. 275.) A number of processes for the analysis of fats, depending upon the power possessed by their unsaturated constituents to absorb by direct addition two or four atoms of bromine or iodine, have been proposed and used, amongst others, by Allen (*Analyst*, vi., 177); Mills and Snodgrass (*Jour. Soc. Chem. Ind.*, ii., 436); Mills and Akitt (*Jour. Soc. Chem. Ind.*, iii., 65); Hübl (*Dingler's Poly. Jour.*, ccliii., 281, and *Jour. Soc. Chem. Ind.*, iii., 641); Levallois (*Jour. pharm. Chim.*, 1887, i., 334); Halphen (*Jour. pharm. Chim.*, 1889, xx., 247); Gantter (*Ztschr. anal. Chem.*, 1893, 178).

The aim of all these processes is to determine the amount of halogen which the substance under examination will absorb by addition, but the figures obtained represent this only approximately even when substances which easily form substitution products are absent. Some substitution takes place with almost all oils, and with rosin-oil, rosin, and probably most other resins, substitution causes the entire absorption.

The extent to which this substitution takes place depends upon the nature of the substance operated upon, and varies with different oils and resins, and a determination of the amount of halogen so absorbed may serve as a means of identifying and in some cases determining them.

The following process has been devised for determining the amount of bromine which oils and resins can absorb by addition (which will be called the "Bromine Addition Figure"), and at the same time the amount of bromine which replaces hydrogen, the action being allowed to continue eighteen hours in the dark; this gives the "Bromine Substitution Figure." The first figure gives in most cases the same information as the Hübl figure, but is more reliable, while the second figure is a measure of the activity of the saturated constituents toward bromine.

It depends upon the fact that bromine, in forming substitution compounds, forms a molecule of hydrobromic acid for every atom of bromine which replaces hydrogen, while in forming addition compounds no hydrobromic acid is formed.

It was found impossible to use iodine alone, as the addition figures are then very much too low, and there is little difference between the substitution figures of bodies of unlike character.

The following solutions are used :

Bromine in carbon tetrachloride	...	...	$\frac{N}{3}$
Sodium thiosulphate	...	...	$\frac{10}{N}$
Potassium hydroxide	...	...	$\frac{10}{N}$

0.250—1.000 gram of the substance is dissolved in 10 c.c. of carbon tetrachloride in a bottle of 500 c.c. capacity provided with a carefully ground glass stopper. An excess of bromine solution is added, the bottle tightly stoppered and placed in a dark closet. No water or alcohol should be present, and light should be excluded as far as practicable. At the end of eighteen hours the bottle is cooled with ice to form a partial vacuum, and a piece of wide rubber tubing about one and one-half inches long is slipped over the lip of the bottle so as to form a well about the stopper. This well is filled with water and the stopper carefully lifted, when the water will be sucked into the bottle and dissolve the hydrobromic acid present. When about 25 c.c. of water have been added in this way, the bottle is well shaken, and 10—20 c.c. of 20 per cent. potassium iodide solution added. The excess of bromine acts on the potassium iodide, liberating a corresponding amount of iodine which is titrated with $\frac{N}{10}$ thiosulphate after adding about 75 c.c. more water, using starch as an indicator. The total bromine absorption is calculated from the difference between the amount of thiosulphate required for the bromine solution added and the amount required for the excess. The contents of the bottle are now transferred to a separatory funnel and the aqueous portion separated, filtered through a cloth filter, a few drops of thiosulphate added if the solution is blue, and this is then titrated with $\frac{N}{10}$ potassium hydroxide, using methyl orange as indicator. The end reaction is best observed by using a porcelain casserole to contain the solution, adding the alkali in slight excess and titrating back with $\frac{N}{10}$ hydrochloric acid until the pink acid tint just reappears. From the number of cubic centimetres of alkali used the amount of bromine present as hydrobromic acid is calculated, and when expressed in per cent. gives the bromine substitution figure, because for every atom of bromine which has replaced an atom of hydrogen, one molecule of hydrobromic acid has been formed. Twice the bromine substitution figure subtracted from the total absorption gives the bromine addition figure.

The following results were obtained :

Substance.	Total bromine absorption, eighteen hours.	Bromine, addition figure.	Bromine, substitution figure.
W. G. Rosin ...	212.7	0.0	106.35
E. Rosin ...	206.5	0.0	103.25
Second run Rosin Oil (a) ...	116.2	0.0	58.1
" " " " (b) ...	114.7	0.0	57.35
American Raw Linseed Oil ...	102.88	102.88	0.0
Same Oil Boiled ...	103.92	103.92	0.0
White Salad Cotton-seed Oil ...	65.54	64.26	0.64
Sperm Oil ...	56.60	54.52	1.04

A consideration of the above figures shows that the results are much more instructive than those obtained by the Hübl process which is the one in common use. Rosin-oil, rosin, and other resins may be detected and determined in mixture with fatty oils, or, if they are present in known quantity, the character of the fatty oil may be determined. Investigations which are being made on a large number of oils and resins will probably furnish analytical data for the analysis of oils and varnishes.

W. J. S.

An improved Volumetric Precipitation Process. P. N. Raikow. (*Chem. Zeit.*, 1894, xviii, 484, 485.)—The cardinal fault of most volumetric precipitation processes is that no direct reading of the end-point is possible, filtration and trial of small portions of the clear filtrate being usually necessary. The author has found that many precipitates which remain obstinately suspended under ordinary conditions, and cause in the liquid being titrated an unmanageable turbidity, can be induced to collect and subside by the addition of some immiscible liquid heavier than water, e.g., carbon disulphide or chloroform. Such liquids, although exerting no solvent action on the precipitate, mix intimately with it and carry it down, leaving the supernatant liquid sufficiently clear for the observation of any turbidity produced by the addition of a further quantity of the standard precipitating solution. Carbon disulphide and chloroform are usually, but not invariably, effective. Thus carbon disulphide carries down silver chloride rapidly and completely, but has no influence on the precipitation of barium sulphate. The application to particular cases of the principle here enunciated is being worked out by the author.

B. B.

REVIEW.

ANIMAL AND VEGETABLE FIXED OILS, FATS, BUTTERS, AND WAXES: THEIR PREPARATION AND PROPERTIES, AND THE MANUFACTURE THEREFROM OF CANDLES, SOAPS, AND OTHER PRODUCTS. By C. R. ALDER WRIGHT, D.Sc., B.Sc., F.R.S., with 144 illustrations. Price 28s. (London: Charles Griffin and Company, Limited.)

This work is one of those which almost defy the reviewer. The vast amount of detail, the numerous tables, and the breadth of the subject, render any concise description of the work difficult, if not impossible.

In his preface, the author admits that the complete discussion of the sources, production, and general technology of the numerous substances included in the term "oils" would require far more space than is compatible with the limits of the work, and hence it has been found indispensable to make a selection, with the result that the subjects are now narrowed down to animal and vegetable fixed oils and allied substances, whilst mineral oils, products of distillation, essential oils, and various analogous materials are only discussed in so far as they are associated with the fixed oils in their technological application. In short, the object aimed at has been rather to give general descriptions of the methods whereby animal and vegetable oils and fat are obtained from natural sources, of their leading practical applications and uses, and of their chief physical and

chemical properties and reactions, than to enter into special details, and to discuss minutely the analytical tests and processes applicable in each separate case for the detection of adulteration.

The author proceeds to express his indebtedness to various scientific and technical journals, and in particular to the works of Schädler, Allen, and Benedikt. The author has culled extensively, yet with discretion, from the treatises of these authors, and with due acknowledgment of the source of his information. Whether the authors of these treatises will appreciate the wholesale conveyance of their tables and subject-matter to Dr. Wright's work is very doubtful, but there can be no question that the readers of the book will be greatly the gainers thereby.

Dr. Wright's compilation appears to be exhaustive, and the result is that his work will be found absolutely indispensable by every chemist interested in the subject of oil and fat analysis. It is refreshing to find a work on technical chemistry edited in a thoroughly scientific manner, and free from the slipshod chemistry which distinguishes some of the more pretentious works recently published.

After treating of the sources and general nature of fixed oils, Dr. Wright proceeds to describe the products of their saponification. Section II. deals with the physical properties of oils, fats and waxes, and the various tests for their purity and identity based thereon. In Section III. the chemical properties of oils, etc., are considered, the processes of general chemical analysis being fully and clearly described. In the fourth section the processes used for extracting, rendering, refining and bleaching oils, etc., are described, and here we have a most valuable compendium of information on a subject on which but little reliable and up-to-date information has hitherto been obtainable. In Section V. the author deals with the classification and uses of fixed oils, etc., and describes their adulterations and the methods of detecting them. Only some of the leading oils are considered in detail, but the information given is concise and reliable. The candle and soap industries are considered in the two concluding sections of the work. Here the author's special knowledge finds full scope.

Altogether, the book teems with information valuable alike to the analyst and the technical chemist. For many pages of the book the reader might suppose he was perusing a new edition of Mr. Allen's well-known volume II., while in other parts the author treats his subject from an entirely different standpoint, and introduces illustrations of manufacturing plant and processes which in themselves are sufficient to secure a warm welcome for the book.

The work is issued with cut leaves, is closely but clearly printed, and fairly free from typographical errors. It concludes with an index covering 45 pages.

APPOINTMENT.

Mr. George R. Thompson, Newport, Mon., has been appointed District Agricultural Analyst for the County of Monmouthshire and the County Borough of Newport.